Selective estragole to trans-anethole isomerization in ionic liquids

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Keywords: estragole, isomerization, ruthenium

INTRODUCTION

Trans-anethole is a naturally-occurring product which has been traditionally extracted from anise or fennel oils, albeit with variable proportions of its cis-isomer as an impurity.1 However, the increasing demand of trans-anethole has made extraction from natural sources not sufficient to supply the market, hence the need to produce it synthetically.2 Effectively, only trans-anethole is interesting for industry since the cis-isomer presents a higher toxicity and unpleasant organoleptic properties. Consequently, the search for efficient and selective catalytic systems able to promote the estragole to trans-anethole isomerization still remains a challenge for synthetic chemists.

RESULTS AND DISCUSSION

Initially, the catalytic activity of complexes PdCl₂(NCPh)₂ (1a), RhCl(PPh₃)₃ (1b) and RuHClCO(PPh₃)₃ (1c) in the isomerization of estragole has been tested. Experiments were performed at 80 °C using 2 mmol of substrate, 0.020 mmol of complex, 0.5 mL of toluene (1a and 1c) or ethanol (1b), and the reaction was monitored by GC analyses of aliquots. The best results were obtained with 1c which quantitatively converted estragole into anethole in 1 h with selectivity in the trans isomer of 95%. We next investigated how the process is affected by changing the catalyst loading. We observed that decreasing the amount of ruthenium (complex 1c) from 0.020 to 0.015 mmol did not modify the trans:cis ratio (95:5). On the other hand, lower metal loadings (0.010 mmol) conducted to lower selectivities in the desired trans-isomer (92%). In an attempt to improve the selectivity, the process has been carried out at lower temperature (35 °C) with the most active complex 1c. The trans-selectivity decreased (81% vs. 95%) and the reaction time dramatically increased (7 h vs. 1 h). The isomerization of estragole has also been tested in different amounts of toluene (0.5, 1.0 and 4.0 mL). Remarkably, complete conversion in only 5 min was observed when 0.5 mL of toluene was employed, with high selectivity in trans-anethole (98%). The next step was the employment of ionic liquids in the estragole isomerization in order to obtain a simple separation of products from the reactional media. Experiments were performed at 80 °C using 2 mmol of substrate, 0.015 mmol of 1c, 0.5 mL of toluene and 0.5 mL of BMI-NTf₂. A conversion of 99% was obtained after 20 min with trans-selectivity of only 87%. Then, ionophilic ligands (Figure 1) were applied in this system to support the catalyst in the ionic phase and allow its recyclability.

Figure 1. Ionophilic ligands employed in isomerization.

The system containing only BMI-NTf₂ has decreased its conversion by reuse of catalytic phase (99% 1st cycle; 50% 2nd cycle; 32% 3rd cycle; 22% 4th cycle), although the selectivity in trans-anethole remains unchanged (87%). Gratifyingly, the system containing the ionophilic ligands (L₁, L₂ or L₃) could be re-used up to three consecutive runs without loss of conversion (>99.5%) and selectivity (96%). However, a decrease of the conversion (>99.5% vs. 91%), accompanied by a slight loss of the trans-selectivity (96% vs. 91%), was observed after the fourth cycle.

CONCLUSION

In summary, the RuHClCO(PPh₃)₃ has shown to be effective catalyst to convert estragole into anethole. The best conversion (>99.5%) and selectivity toward trans-anethole (98%) were obtained with 0.015 mmol of this precursor, 0.5 mL of toluene, 80 °C and 5 min of reaction. Furthermore, the system containing BMI-NTf₂ and ionophilic ligands showed to be a good alternative to recycle the catalyst with high conversions (>99.5%) and high trans-selectivities (96%).

ACKNOWLEDGEMENTS

Thanks are due to the following agencies for financial support: CNPq, CAPES and PETROBRAS.

REFERENCES